

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE September 7, 1995		3. REPORT TYPE AND DATES COVERED
4. TITLE AND SUBTITLE Simulation of the vibrational overtone activation of methylcyclopropene			5. FUNDING NUMBERS N00014-95-1-0452	
5. AUTHOR(S) I.Ouporov, D.L.Snaveley and O.Grinevich				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Center for Photochemical Sciences Bowling Green State University Bowling Green, OH, 43402			8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report 4	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Program 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public Release: distribution unlimited			12b. DISTRIBUTION CODE	
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14. SUBJECT TERMS Monte-Carlo and Master Equation simulation, vibrational overtone activation, RRKM theory, unimolecular reaction			15. NUMBER OF PAGES 28	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-95-1-0452

R&T Code 4131063

Technical Report No. 4

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by

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Prepared for Publication

in

Journal of Physical Chemistry

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Sept. 5, 1995

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Simulation of the Vibrational Overtone Activation of Methylcyclopropene

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Abstract

The complete kinetic data for the vibrational overtone activation of methylcyclopropene have been simulated using a combination of master equation and Monte Carlo procedures. The simulation included photoactivation, collisional energy transfer and reaction into three unimolecular channels. A good fit to the Stern-Volmer plots for all the products at six different photolysis energies was obtained. The fit required an adjustment of the thermal activation barriers input into the RRKM calculation. The best fit barriers were: 12,833 cm^{-1} for 2-butyne, 14,547 cm^{-1} for 1,3-butadiene and 14,685 cm^{-1} for 1,2-butadiene. The collisional deactivation was fit with a single exponential energy transfer distribution function with an average amount of energy transferred per collision of 1000 cm^{-1} . This average value fit all of the Stern-Volmer plots. The product yield ratios were examined for local mode specific effects, but none were found. Stern-Volmer plots were constructed for methyl cyclopropene diluted in helium, argon and sulfur hexafluoride for the $\Delta v = 6$ olefinic CH stretch transition. These plots were simulated using the same calculation parameters as above except for those having to do with the collider gas. For these simulations the average amounts of energy transferred were 150, 200 and 500 cm^{-1} for helium, argon and sulfur hexafluoride, respectively.

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Introduction

In the investigation of the role of vibrational energy in unimolecular reactions the inherent difficulty with thermal activation is the wide energy distribution produced so that measured quantities are averaged over the population distribution. Averaging can result in the failure of such experiments to differentiate specific effects arising from activation, collisional deactivation or the actual reaction step. The method of photoactivation called vibrational overtone activation¹, selectively populates vibrational overtone states using visible laser light, producing a narrow energy distribution of activated molecules. The molar extinction coefficients for these transitions are about 10^{-4} ; therefore, the sample must be irradiated inside the laser cavity where the photon density is high.

Product yields in vibrational overtone activation experiments are the result of the competition between collisional deactivation and reaction. Because the energy distribution of the activated molecules is narrow it has been assumed that direct comparisons can be made between the experimental specific rate coefficients obtained from the slope of the Stern-Volmer plot². In a recent example, the vibrational overtone activation of the isomerization of methyl isocyanide using seven strategically chosen photolysis wavelengths yielded experimental specific rate coefficients which exactly correspond to the calculated RRKM rates³. The wavelengths were chosen to test if several mechanisms were operant in determining the specific rate coefficient. First, the peak maxima for the $5\nu_{CH}$ and $6\nu_{CH}$ transitions were photolyzed to determine the overall energy dependence of the specific rates. In addition, wavelengths to the red and blue of the peak maxima (but still within the band contour width) were photolyzed to test for rotational and/or vibrational effects. In every case the experimental specific rate coefficient increased monotonically with energy as predicted by RRKM theory.

These types of comparisons work well at high pressure but fail at low pressure, because they do not take into account the pressure dependence of the collisional deactivation process. For example the Stern-Volmer plots for the isomerization of methyl isocyanide curve at low pressure³. Negative curvature (decreasing slope with increasing pressure) was observed in the $5\nu_{CH}$ excitation and positive curvature (increasing slope with increasing pressure) was observed in the $6\nu_{CH}$ excitation.

Through the master equation calculation⁴ a more complete understanding of the processes producing the product yields was available⁵ so that the low pressure curvature could be

¹Crim, F.F. *Ann.Rev.Phys.Chem.* **1984**, 35, 367.

²Reddy, K.V.; Berry, M.J. *Chem.Phys.Lett.* **1977**, 52, 111.

³Hassoon, S.; Rajapakse, N.; Snively, D.L. *J.Phys.Chem.* **1991**, 96, 2576.

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⁴Chandler, D.W.; Miller, J.A. *J. Chem. Phys.* **1986**, 85(8), 4502.

⁵Chandler, D. W.; Miller, J.A. *J. Chem. Phys.* **1984**, 81(1), 455.

understood. The master equation calculation takes into account the energy distributions, the energy transfer probability functions and the energy dependence of the reaction rate constant. This curvature occurs because at low pressure the initial distribution of activated molecules (the room temperature Boltzmann distribution shifted up by the photon energy) is also the reactive distribution. In other words, all of the initially excited molecules react. At high pressure the reactive distribution shifts to lower energy for the $6\nu_{CH}$ transition, a natural trend of the collisional deactivation process, but shifts to higher energy for the $5\nu_{CH}$ transition. The reactive distribution for the $5\nu_{CH}$ transition shifts to higher energy because of the close proximity of the reaction barrier. At high pressures near the reaction barrier only the most energetic activated molecules react so the measured rate constant is larger than that measured at low pressure. This creates curvature in the Stern-Volmer plots.

The work described here is a simulation of the vibrational overtone activation⁶ of gaseous methylcyclopropene. Under irradiation of specific vibrational overtone transitions in methylcyclopropene the ring opening reaction occurs to produce three products: 2-butyne, 1,3-butadiene and 1,2-butadiene^{7,8}. The optical transitions used corresponded to the fourth and fifth vibrational overtones of the methylenic, methyl-in-plane and vinyl CH local mode stretches. The measured specific rate coefficients for the three unimolecular reactions were determined and compared to calculated rates from RRKM theory. To date vibrational overtone activation experiments simulated by master equation calculations have only one possible unimolecular product. The work presented here simulates a vibrational overtone activation reaction with multiple reaction channels.

Vibrational overtone activation involves a timed photolysis period during which some of the molecules absorb a photon and undergo chemical reaction. The amount of product formed is determined by gas chromatography. These experimental data are typically plotted as the inverse apparent yield versus pressure. The apparent yield is the individual product yield as determined by chromatography divided by the photolysis time and the laser power. In the case for the reaction of methylcyclopropene the yields for all three products were determined at each photolysis wavelength and each pressure.

The general mechanism for the vibrational overtone activation of MCPene begins with the photoactivation step.

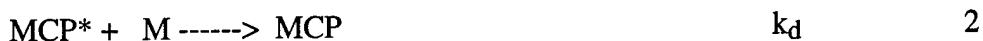


⁶Technical Report Number 15

⁷Srinivasan, R. *J. Am. Chem. Soc.* **1969**, 91, 6250.

⁸Hopf, H.; Wachholz, G.; Walsh, R. *Chem. Ber.* **1985**, 118, 3570.

The population distribution of activated molecules in this step is assumed to be a thermal distribution at room temperature but displaced by the photon energy for the photolysis. Compared to the population distribution typical in thermal activation experiments this is quite narrow. After the molecule has been "pumped" into the upper state, it can either deactivate through collision or pass over the reaction barrier to collisionally deactivate to the ground state of the product. In the first case no chemical reaction occurs.



The second step is the chemical reaction to form the three products



characterized by the specific unimolecular rate coefficients, k_1 , k_2 and k_3 , respectively. As described by the RRKM theory these constants depend only on the total internal energy. It is clear from the spectroscopic evidence that the photon initially excites only the stretch states; however, the energy is quickly randomized throughout the molecule. We are testing to see if it is possible to create activated MCP molecules with vibrational excitations which will promote the creation of one product over another.

Experimental Data and Previous Comparison to RRKM Calculation

The ring opening of MCPene was activated using six different absorption features including three types of CH stretches (methyl, methylenic and olefinic) in the $5\nu_{\text{CH}}$ and $6\nu_{\text{CH}}$ transitions⁶. The wavenumbers and assignments of these six photolyses are listed in Table 1. The experimental gas chromatography integrated areas from which the product ratios were derived were calibrated with primary standards purchased from Aldrich Chemical Co. The product yield ratios for a particular photolysis energy should be reproduced by the simulation. Stern-Volmer plots for each product were constructed. For the lower overtone transition only 2-butyne was produced since the activation barrier for the butadienes was higher in energy.

Our previous work on this system, as described in Technical Report No. 15, involved simple comparisons of the experimental specific rate coefficients to an RRKM calculation which used Gilberts UNIMOL SUITE (1992 version). This calculation was performed with no rotational degrees of freedom, Baggott's vibrational frequencies and the Whitten-Rabinovitch state counting procedure. The experimental rates were derived from the experimental slope and

intercepts using a hard sphere collision model. Although this comparison was good, there were specific problems. The RRKM and experimental rate coefficients for 2-butyne on average varied by a factor of 2. These averages for 1,3-butadiene and 1,2-butadiene were 0.98 and 1.43, respectively. For 2-butyne there was closer agreement at higher excitation energy. For the lowest two energies the experimental rate coefficients were factors of 2.3 and 5.5, respectively, higher than the RRKM rates, while the highest two energies were factors of 1.7 and 0.91 higher. Furthermore the experimental relative product yields could not be reproduced with this RRKM calculation with the relative yield of 2-butyne being too high.

Simulations

The experimental and best fit Stern-Volmer plots are shown in Figures 1 through 6. These plots represent the disappearance of the reactant. For the three lowest photolysis wavelengths the only product formed was 2-butyne. For these three plots the disappearance of reactant occurs at the same rate as the appearance of product. Figures 7 through 9 show the experimental and simulated data for the appearance of the three products at the three highest photolysis wavelengths. These simulations reproduce the product yield ratios at each photolysis energy and the Stern-Volmer slopes.

Two computer programs were used for these simulations: Jackson's master equation approach⁹ at the two lowest photolysis energies and Barker's Monte Carlo procedure^{10,11} at the higher energy photolyses. Jackson's program was preferred at low energy when a small fraction of the activated molecules react. Under these low reaction conditions Barker's method required a large number of trajectories to reach the required accuracy. However at higher energy Monte Carlo procedure became ideal for reproducing the competition between collision and the three reactive channels.

Barker's program implements a Monte Carlo procedure to determine the fate of an energized molecule. The effect of collisional deactivation, collisional activation and reaction into as many as three products are considered. Energy dependent rate constants are used to determine the probabilities of a molecule possessing a certain amount of energy undergoing a reactive or collisional event. Each trajectory simulates a random walk for a single molecule. Then the outcomes of many trajectories are averaged to obtain the product yields. The precision of the calculated yields is proportional to $N^{1/2}$ where N is the number of trajectories. At low energy and high pressure as many as 8000 trajectories were run in our calculations to achieve a suitable precision of 3-5%.

⁹Quantum Chemistry Program Exchange, Program No. 104 by R.L.Jackson.

¹⁰Barker J.R. *J. Chem. Phys.* **1980**, 72(6), 3686.

¹¹Barker J.R. *Chem. Phys.* **1983**, 77, 301.

Jackson's program solves a time-dependent master equation which describes the behavior of a microcanonical ensemble of molecules. Differential equations describe several simultaneous processes such as photoactivation, collisional energy transfer and the possible reaction steps. The input file requires all the experimental conditions, some molecular parameters and a description of the energy transfer function. The output provides the percent conversion of the reactant. It should be noted that the experiment cannot be simulated exactly. In Jackson's program the photoexcitation must be described as a pulse of light. For our continuous-wave experiment, photolysis times were longer than one hour so that our "pulse" was exceedingly long. This long pulse dramatically increased the calculation time. To shorten the calculation time we experimented with shorter, high intensity pulses. The shape and energy maximum of the reactive distribution did not change significantly even when the light fluence increased by a factor of 10^5 . In other words, the number of excited molecules after this increase in the fluence was still too small to affect the reactive distribution. This allowed us to describe the 1 to 6 hour experiments as high intensity pulses with 10^{-3} - 10^{-2} s durations.

Both programs require the density of states as input and either the sum of states (Barker's program) or RRKM rate data (Jackson's program). A new RRKM calculation was undertaken in order to refine the fit of the experimental plots. Table 2 gives the new vibrational frequencies. These frequencies were varied keeping the dS_{vib} constant at 12.80. The 200 cm^{-1} mode used in the previous calculation was removed and methyl rotors were used for the energized molecule. Methyl rotors were also included for the transition states. Calculating the density of states at lower energies, close to the barrier, is particularly critical in the overtone experiment simulation. Barker's program uses a 25 cm^{-1} grain size for the first 2500 cm^{-1} and then switches to a grain size of 100 cm^{-1} . This allows for a closer counting of the vibrational states so that the change in the specific rate coefficient with energy reflects the finer detail of the density of states.

We estimated the rotational constants for the transition state using Spartan from Waveform. The C-C bond which breaks during the reaction was arbitrarily stretched to 2 \AA to simulate the geometry of the transition state. The rotational constants for this geometry were 93.1 and $312.5\text{ \AA}^2/\text{amu}$ (for the reactant) and, 93.4 and $374.0\text{ \AA}^2/\text{amu}$ (for the transition state). These values were used in the RRKM calculation. Although there was no experimental evidence indicating that this was the correct choice, we believe that this structure is reasonable for the transition state structure.

After adjusting the vibrational frequencies a final adjustment to the activation barriers was made. The decision to do this was motivated by low yields for all the products in the simulations so far. There were two ways to increase the product yield - either decrease the barrier or decrease the average amount of energy transferred in collisions. The second parameter does not influence the product ratios as much as the first one. A relatively large adjustment was in

order to fit the experimental results so we adjusted the barriers first. We believe that the experimental product ratios should be taken as a starting point in this procedure. The experimental product ratios were determined by gas chromatography with high accuracy since depend neither on the laser power nor on the GC conditions. We lowered the activation barriers keeping within the lower limits of the experimental error from the thermal activation experiments⁸. However the final best fit required even larger changes. These are reported in Table 2. The largest change was for 2-butyne for which the barrier was dropped 325 cm⁻¹, a change of 2.5 %. For 1,3-butadiene and 1,2-butadiene the changes were less than 1% and 2%, respectively, within the experimental error of the thermal measurements⁸. The averaged experimental and calculated product ratios obtained after these barrier changes are summarized in Table 1.

Both Barker's and Jackson's programs calculate the fraction of activated molecules which form products. Command files were created to run these programs at the necessary pressures and construct Stern-Volmer plots from the output data. The construction of the Stern-Volmer plots required absorption cross sections, σ , for the vibrational overtone transitions. A spectroscopic and a kinetic approach were both used to arrive at numerical values for σ . The absolute absorption cross section for the absorption at 17,093 cm⁻¹ was reported by Baggott using a comparison to cyclobutene¹². Using this value the absolute cross sections for all the other absorptions can be obtained by ratioing the absorption strengths of the individual bands to that of the 17,093 cm⁻¹ absorption. The MCP spectrum from 12,645 to 14,367 cm⁻¹ and 15,484 to 14,367 cm⁻¹ (Pyridine 2 and Rhodamine 6G dye regions) were previously recorded by Samarasinghe and Snavely¹³. With the recording of the spectrum from 14,350 to 15,900 cm⁻¹ (DCM dye region) shown in Figure 10, the spectrum of 5v_{CH} and 6v_{CH} overtone transitions is complete. In order to determine the relative strengths of these transitions the overlapping methyl and methylenic peaks were deconvoluted using Lorentzian band profiles. They were deconvoluted by a program based on the Marquardt method¹⁴ into three band contours belonging to the methylenic, methyl-out-of-plane and methyl-in-plane hydrogen vibrations. The following intensity ratios for the methylenic (m), methyl-in-plane (mip) and olefinic (o) peaks were determined for the fourth (4) and fifth (5) overtones: m(4) : mip(4) : o(4) : m(5) : mip(5) : o(5) = 45.8 : 18.8 : 12.3 : 3.7 : 1.5 : 1.

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¹²Baggott, J.E.; Law, D.W. *J. Chem. Phys.* **1988**, 88(2), 900.

¹³Samarasinghe, S.; Snavely, D.L. *Chem. Phys. Letters* **1988**, 150(5), 386.

¹⁴*Fundamentals of process analysis and simulation*: Bischoff, K.B.; Himmelblau, D.M.; American Institute of Chemical Engineers: New York: 1967.

In theory a comparison of the photoacoustic spectral intensities of other peaks to the olefinic peak would yield approximate absolute cross sections for the other photolysis energies. Unfortunately, in practice this comparison involved too many approximations to be satisfactory for our work. The photoacoustic signal is proportional to the pressure changes in the cell due to the absorption of light and does not follow Beers law. The comparison of relative intensities involving different laser dyes posed the largest problem.

To avoid the problems inherent in the photoacoustic method, the true absorption spectrum was recorded in a conventional spectrometer. Figure 11 represents the average of three runs taken by a Varian 104 spectrometer in a 1 cm cuvette being maintained at 0 °C. The strong peak at 722 nm is believed to belong to the methyl stretch ($\Delta\nu=5$) shifted by 268 cm^{-1} to the blue of the gaseous peak by the liquid environment. The liquid spectrum does not resolve the methyl-out-of-plane or in-plane stretches but does give a reliable ratio for absorption cross sections for the olefinic and other hydrogen stretches. The derived ratio was: $m(4) : mip(4) : o(4) = 4.9 : 2.9 : 1$.

The second approach to the determination of σ involves calculating absorption cross sections from the Stern-Volmer intercepts. σ can be derived by the following equation¹⁵ :

$$\sigma = k_a/c = (c I)^{-1} \quad 6$$

where k_a is the activation rate constant, c is speed of light and I is the Stern-Volmer intercept. The error of each rate determination and any systematic error in the laser power calibration affect the value of the experimental intercept. In addition the larger the Stern-Volmer slope the larger the error in the intercept measurement. The Stern-Volmer plots for low energy photolyses possess larger slopes which in turn creates larger errors in the intercept. One inaccurate rate measurement for the 13359 and 13582 cm^{-1} photolyses can alter the intercept measurement while the Stern-Volmer intercepts of higher energy photolyses are more reliable. The following ratios were determined from the Stern-Volmer plots : $m(4) : mip(4) : o(4) : m(5) : mip(5) : o(5) = 7.0 : 1.3 : 2.6 : 0.50 : 0.14 : 1$. Absolute values for the absorption cross sections (in cm^{-1}) derived from these kinetic ratios are listed in Table 3. These values were used in equation 6 to calculate the intercepts used in the simulations.

The form of the energy transfer function can be varied in these calculations to test which energy transfer function fits the Stern-Volmer plots best. The average energy transferred per collision can be determined for a particular energy transfer function³. For the collisional energy transfer process, a Lennard-Jones collision diameter, σ_i , of 5.17\AA and a Leonard-Jones collision parameter, ϵ_i , of 344 K were calculated using semiempirical relationships¹⁶. The critical

¹⁵Baggot, J.E.; Law, D.W. *J.Phys.Chem.* **1986**, 85(11), 6475.

³

¹⁶Stiel, L.I.; Thodos, G. *J.Chem.Eng.Data* **1962**, 7(2), 234.

parameters for methylcyclopropene were obtained by comparison with those for the cyclic and acyclic C₄ hydrocarbons¹⁷. The critical volume and temperature respectively were 206Cc./G.-Mole and 557K. The collision parameters for all the calculations are listed in Table 4.

Calculations were undertaken with two different energy transfer functions, $P_i(E, E')$, which describes the probability that a molecule with energy E will undergo a collision to energy E' to $E' + dE'$. The single exponential down function is described by ¹¹

$$P_{di}^e(E, E') = \exp(-(E-E')/\alpha) / N(E)$$

for down transition where $E' < E$ and

$$P_{ui}^e(E, E') = \rho(E')/\rho(E) [\exp((E-E')/\alpha) / N(E')] \times [\exp((E-E')/k_B T)]$$

for up collisions where $E' > E$. In these expressions α is the average amount of energy transferred in down collisions, $N(E)$ is a normalization factor, $\rho(E)$ is the density of states, and k_B is Boltzmann's constant. The Poisson distribution was also used. It is described by⁹

$$P_{di}^p(E, E') = [(E-E')/(\alpha N(E))] \times [\exp(-(E-E')/\alpha)]$$

for down transition where $E' < E$ and

$$P_{ui}^p(E, E') = [\rho(E')/\rho(E)] \times [\exp((E-E')/\alpha)] \times [\exp((E-E')/k_B T)] \times [(E'-E)/(\alpha N(E'))]$$

for up collisions where $E' > E$. Because no significant difference in the calculation was observed for these two possibilities, the single exponential down function was used at all photolysis energies due to its simplicity of interpretation. Attempts were made to fit the experimental data with various α in the range of 500 to 1600 cm⁻¹. Although the slopes of the Stern-Volmer plots did not depend strongly on α over this range we believe that 1000 cm⁻¹ gave the best fit. This value is reasonable for a C₄ hydrocarbon¹⁸. Previously, Baggot and Law¹² derived $\alpha=730$ cm⁻¹ for the disappearance of MCPene at 17093 cm⁻¹ using the master equation method. In our simulations 730 cm⁻¹ was clearly too small a value. The disagreement here probably arises from our improved choices of activation barriers and the smaller changes in the RRKM vibrational frequencies which were made in order to fit all of our data.

After simulating the pure MCPene photolyses, gas dilution experiments were performed and simulated to test the parameters used in the simulation. Experimental conditions were kept essentially the same except that MCPene was diluted 1:15 in bath gases (He, Ar, SF₆) and the 17,093 cm⁻¹ was the only excitation wavelength. The Stern-Volmer plots for the reactant disappearance are shown in Figures 12-14. The slopes of the lines decrease due to the weak collider effect. The collider efficiencies were calculated by ratioing the the Stern-Volmer slope

¹⁷CRC Handbook of Chemistry and Physics; Weast, R.C., Ed.; CRC press, 54th edition.

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¹⁸Oref, I.; Tardy, D.C. *Chem. Rev.* **1990**, 90, 1407.

¹²

divided by the intercept. The estimated values were compared to the efficiencies obtained from the thermal methylisocyanide isomerization data and found to be in good agreement¹⁹. The values are summarized in Table 5. In the simulations it was assumed that "hot" molecules only collide and transfer energy to the bath molecules. The only changes in the input parameters were the collider characteristics (Table 4) and the average amount of energy transferred per collision. The calculated and experimental product ratios were found to be in good agreement. They are presented in Table 1. Both theoretical calculations and experiments show the decrease of the relative yield of 2-butyne. The 1,3-butadiene/2-butyne ratio increases from 0.21 to 0.28 due to the dilution in bath gas. The best fit was obtained for $\alpha=150\text{ cm}^{-1}$ (He), $\alpha=200\text{ cm}^{-1}$ (Ar), $\alpha=500\text{ cm}^{-1}$ (SF₆).

Conclusion

The kinetic data for the ring opening of methylcyclopropene activated by vibrational overtone excitation have been simulated using two approaches: a master equation process and a Monte-Carlo method. The Monte-Carlo approach applied for the high energy reactive distribution where several products are formed. Accurate results were achieved by simulating as many as 8000 trajectories for the highest pressure used in the experiment. The master equation technique was preferred when the reactive distribution was close in energy to the barrier and only one product was formed. The final fit required adjustment of the isomerization barriers for all three products. The barrier for the production of 2-butyne was lowered 325 cm^{-1} from the thermal barrier, a change of 2.5%. The barriers for 1,3-butadiene and 1,2-butadiene were also lowered but only by 1 and 2%, respectively. The average amount of energy transferred per collision for self collision was 1000 cm^{-1} . Several dilution experiments were performed in order to test the goodness of our parameters. The average amount of energy transferred per collision decreased when MCPene was diluted in the less efficient colliders gases such as Ar, He, SF₆. Moreover, theoretical and experimental product ratios agree which makes us more confident that the adjustment has been done correctly. The isomerization of MCPene demonstrates only statistical behavior.

¹⁹Chan, S.C.; Rabinovitch, B.S.; Bryant, J.T.; Spicer, L.D.; Fujimoto, T.; Lin, Y.N.; Pavlou, S.P. *J.Phys.Chem.* **1970**, 74(17), 3160.

Table 1 Photolysis Wavenumbers, Assignments and Experimental (*Calculated*) Product Ratios

Wavenumber, cm ⁻¹		2-butyne	1,3-butadiene	1,2-butadiene
13359	5-0 methylenic	1.0 (1.0)	-	-
13582	5-0 methyl-in-plane	1.0 (1.0)	-	-
14552	5-0 olefinic	1.0 (1.0)	-	-
15623	6-0 methylenic	0.886 (0.864)	0.091 (0.092)	0.023 (0.044)
15895	6-0 methyl-in-plane	0.881 (0.849)	0.083 (0.104)	0.036 (0.047)
17093	6-0 olefinic	0.762 (0.755)	0.171 (0.162)	0.067 (0.083)
17093	6-0 olefinic (in He)	0.739 (0.742)	0.209 (0.212)	0.052 (0.046)
17093	6-0 olefinic (in Ar)	0.741 (0.736)	0.208 (0.210)	0.051 (0.054)
17093	6-0 olefinic (in SF ₆)	0.745 (0.751)	0.201 (0.197)	0.054 (0.052)

Table 2 Vibrational Frequencies for RRKM Calculation

Reactant	Deg.	2-butyne	Deg.	1,3-butadiene	Deg.	1,2-butadiene	Deg.
3000	2	2800	5	3000	5	3000	5
2950	1	1650	2	1600	2	1600	2
2900	2	1475	3	1450	3	1450	3
2850	1	1275	4	1100	4	1100	5
1650	1	1175	3	1050	5	1050	1
1550	1	1100	2	1000	1	1000	3
1450	2	1075	2	950	1	500	2
1400	2	500	1	450	1	400	1
1100	1						
1050	2						
1000	2						
900	2						
750	1						
700	1						
600	1						
400	1						

Activation Barriers (cm ⁻¹)	2-butyne	1,3-butadiene	1,2-butadiene
Thermal Barrier	13,158	14,661	14,949
Barrier, This work	12,833	14,547	14,685

Table 3 Absolute Absorption Cross Sections for Vibrational Overtone Transitions

$\Delta v = 5$		$\Delta v = 6$	
methylenic	2.13×10^{-24}	methylenic	1.52×10^{-25}
methyl-in-plane	4.00×10^{-25}	methyl-in-plane	4.12×10^{-26}
olefinic	8.00×10^{-25}	olefinic	3.06×10^{-25}

Table 4 Lennard-Jones collision parameters

	σ_i (Å)	ϵ_i (K)
MCPene	5.17	344
He	4.3	72
Ar	5.0	244
SF ₆	7.2	245

Table 5 Collider efficiencies (1.00 for self-collider)

Gases	Experimental value	Taken from Ref.19
He	0.12	0.171
Ar	0.13	0.120
SF ₆	0.51	0.42

